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Atomic Interaction at Distances Smaller than 5×10^{-9} Centimeters

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When atoms having a relative velocity much smaller than 10^8 cm/sec collide, the state of the electrons changes adiabatically in such a way that their energy depends only on the distance R and the initial conditions. In this case, the motion of the atomic nuclei can be described as a motion with the potential energy

$$U(R) = \frac{Z_1 Z_2}{R} e^2 + E(R), \tag{1}$$

where the first term on the right-hand side is the Coulomb interaction between nuclei having charges $Z_1 e$ and $Z_2 e$, and the second term is the total energy of the electrons minus their energy when $R \to \infty$.

Despite the relatively small velocity of the nuclei, the energy of their relative motion can be very large in comparison with the energy of the valence electrons due to the large size of the reduced mass $M_1 M_2/(M_1 + M_2)$. If a considerable scattering of the colliding atoms is to take place, they must approach until R is so small (when $U(R)$ becomes of the order of the energy of the relative motion of the nuclei) that the electron shells of both atoms almost entirely overlap.

According to the Thomas-Fermi statistical model, the total energy of the electrons in an atom is $-0.77\, me^4 Z^{7/3}\hbar^2$ (the empirical value of the numerical coefficient is about 0.6). Hence, at the minimum distance of approach ($R = 0$), $E(R)$ is

$$E(R)|_{R\to 0} = -0{,}77 \frac{me^4}{\hbar^2}\left([Z_1 + Z_2]^{7/3} - Z_1^{7/3} - Z_2^{7/3}\right). \tag{2}$$

Hereafter we shall use the approximate formula

$$(Z_1 + Z_2)^{7/3} - Z_1^{7/3} - Z_2^{7/3} \cong \frac{7}{3} Z_1 Z_2 (Z_1 + Z_2)^{1/3}. \tag{3}$$

This formula gives a maximum error of 4 percent (for $Z_2 \sim 1/3 Z_1$), which is smaller than the error in (2) itself. Then, limiting ourselves to the first term of the expansion of $E(R)$ in powers of R and substituting in (1), we obtain

$$U(R)|_{R\to 0} \approx \frac{Z_1 Z_2 e^2}{R}\left(1 - 1{,}8\,[Z_1 + Z_2]^{1/3} \frac{me^2}{\hbar^2} R + \ldots\right). \tag{4}$$

Formula (4) can be used, for instance, to determine the minimum distance of approach of the colliding atoms when the distances

$$R \ll \frac{1}{1{,}8\,(Z_1+Z_2)^{1/3}}\,\frac{\hbar^2}{me^2} \tag{5}$$

are of importance.

Often, however, (4) is not sufficient and we must, even if only approximately, determine $E(R)$ in (1) over the range of R, where $U(R)$ is of the order of the energy of the relative motion of the colliding atoms.

The change in the energy of the electrons $E(R)$, when the nuclei with the charges Z_1e and Z_2e draw away from each other to the distance R, may be determined as the change in the energy of the electrons of the atom with the nuclear charge $((Z_1+Z_2)e)$, when a charge $+Z_2e$ is placed at a distance R from its center and a charge $-Z_2e$ is placed in the center. Then, in the first approximation of perturbation theory (if applicable), the change in the energy of the electrons equals the product of the charge Z_2e times the average difference of potential produced by the unperturbed electrons between the distances $r = R$ and $r = 0$ from the center of the atom, i.e.,

$$U(R) \simeq \frac{Z_1Z_2e^2}{R} - 1{,}8\,(Z_1+Z_2)^{1/3}Z_1Z_2\frac{me^4}{\hbar^2} - Z_2e\,(\varphi_1(0)-\varphi_1(R)). \tag{6}$$

We know that the criterion of applicability of perturbation theory during the scattering of an electron which has the velocity v relative to a Coulomb center with charge Z_2e is

$$\frac{Z_2e^2}{\hbar v} \ll 1. \tag{7}$$

In this case it is important that the Coulomb field of the charges Z_2e and $-Z_2e$ at distances larger than R decreases more rapidly than R^{-1}. Therefore we shall use (7), substituting as $1/v$ the average value of this quantity at the position of the Z_2e charge.

In the statistical model of the atom, the average value of $1/v$ is

$$\frac{1}{v} = \frac{3m}{2\hbar\,(3\pi^2 n)^{1/3}}, \tag{8}$$

where n, the average number of electrons per unit volume, is determined through the Thomas-Fermi potential $\varphi(R)$:

$$e\varphi(R) = \frac{(Z_1+Z_2)\,e^2}{R}\,\chi\left([Z_1+Z_2]^{1/3}\frac{me^2}{\hbar^2}R\right) = \frac{\hbar^2}{2m}\,(3\pi^2 n(R))^{2/3}; \tag{9}$$

$$\chi(x) = 1 - 1{,}8\,x + 1{,}6\,x^{3/2} - \ldots \sim \frac{100}{x^3}$$

is a universal function. (Usually, the function $\chi\left(\frac{x}{0{,}885}\right)$ is used, i.e.,

$$\chi(x) = 1 - 1{,}59\,x + \frac{4}{3}\,x^{3/2} - \ldots \sim \frac{144}{x^3}.\Big)$$

From (9), (8), and (7) we have the inequality

$$(Z_1+Z_2)^{1/3}\frac{me^2}{\hbar^2}R \ll \frac{8}{9}\,\frac{(Z_1+Z_2)^{4/3}}{Z_2^2}\,\chi\left([Z_1+Z_2]^{1/3}\frac{me^2}{\hbar^2}R\right). \tag{10}$$

Inequality (10), solved with respect to R, may be approximately expressed for existing values of Z_1 and Z_2 by the formula

$$R \ll \frac{5 \cdot 10^{-9} \text{ см}}{(Z_1 + Z_2)^{1/3}} \left(\sqrt[3]{1 - \frac{3 (Z_1 + Z_2)^{2/3}}{Z_2^2}} - 1 \right). \tag{10a}$$

For $Z_2 = 1$ and $Z_1 = 63$, the formula (10a) gives $R \ll 10^{-8}$ cm.

The potential $\varphi_1(R)$ produced by the electrons at the distance R from the nucleus is the Thomas-Fermi potential $\varphi(R)$, which is found from (9), minus the Coulomb potential produced by the nucleus, i.e.,

$$\varphi_1(R) = \frac{(Z_1 + Z_2)\, e}{R} \left\{ \chi \left([Z_1 - Z_2]^{1/3} \frac{me^2}{\hbar} R \right) - 1 \right\}. \tag{11}$$

Thus, the expression for the change in the energy of the electrons in (6) is, in accordance with (11),

$$- Z_2 e (\varphi_1(0) - \varphi_1(R)) =$$

$$= (Z_1 + Z_2)\, Z_2 e^2 \left\{ 1{,}8\, (Z_1 + Z_2)^{1/3} \frac{me^2}{\hbar^2} + \frac{\chi \left([Z_1 + Z_2]^{1/3} \frac{me^2}{\hbar^2} R \right) - 1}{R} \right\}. \tag{12}$$

The expression (12) is not symmetrical with respect to Z_1 and Z_2, although it should be according to the definition given above. The discrepancy is due to the fact that we are limiting ourselves to the first approximation of perturbation theory, which here is an expansion of $E(R)$ in powers of $Z_2/(Z_1 + Z_2)$. Therefore, the first approximation can be used as long as $Z_2/(Z_1 + Z_2)$ is small. However, within the limits of applicability of the first approximation, it is always possible to add or subtract a quantity of second order, i.e., to use $Z_1 Z_2$ instead of $(Z_1 + Z_2)Z_2$ as the factor in front of the curly bracket in (12). On the other hand, when $Z_2/(Z_1 + Z_2)$ approaches unity, it is obvious that (12) must go over into the same expression when Z_2 is replaced by Z_1 and vice versa. In this case, $(Z_1 + Z_2)Z_1$ can be again replaced by $Z_1 Z_2$, this time because of the smallness of $Z_1/(Z_1 + Z_2)$.

Thus, replacing the factor $(Z_1 + Z_2)Z_2$ by $Z_1 Z_2$ in (12) and substituting (12) into (6), we obtain

$$U(R) = \frac{Z_1 Z_2 e^2}{R} \chi \left([Z_1 + Z_2]^{1/3} \frac{me^2}{\hbar^2} R \right). \tag{13}$$

From what was said above, (13) is valid when $Z_2 \ll Z_1 + Z_2$ and when $Z_2 \approx Z_1 + Z_2$, i.e., $Z_1 \ll (Z_1 + Z_2)$.

Limiting ourselves to the first two terms of the expansion of (13) in powers of R, we obtain (4), which, within the limits of its applicability, is valid for any Z_1 and Z_2, including $Z_1 \approx Z_2$. Moreover, if, after taking into consideration the second approximation of perturbation theory, a precise formula could be obtained, the form of the term of second order relative to $Z_2/(Z_1 + Z_2)$ (because of the above-mentioned considerations of symmetry) could only be such that in the formula (12) the factor $(Z_1 + Z_2)Z_2$ could be replaced simply by $Z_1 Z_2$ (since (12) > 0 and the correction of the second approximation to the energy of the ground state is always negative, (12) decreases in any case). These considerations enable us to assume that (13), which is obtained after symmetrization of (12) on Z_1 and Z_2 (the substitution of $Z_1 Z_2$ for $(Z_1 + Z_2)Z_2$), gives an approximately correct interpolation also for the case $Z_2 \approx Z_1$.

It must be noted that, at first glance, in view of (10), Eq. (12) must remain valid in its original form for sufficiently small R's and for $Z_2 \approx Z_1$. Here, however, according to (10), we must have

$$R \ll \frac{4}{Z_1 + Z_2} \frac{\hbar^2}{me^2}.$$

But in this region, it is impossible to use the statistical model of the atom, and consequently the criterion (10) and Eq. (11) are limited according to the applicability of the statistical model by the inequality

$$\frac{1}{Z_1 + Z_2} \frac{\hbar^2}{me^2} \ll R \ll \frac{\hbar^2}{me^2}.$$

The substitution of the exact value of $(\varphi_1(0) - \varphi_1(R))$ would also obviously lead to a formula nonsymmetrical with respect to Z_1 and Z_2, but this only proves that the applicability of the first approximation of perturbation theory, for $Z_2 \approx Z_1$ at least, is marginal for any R. The fact that (12) cannot be valid for

$$R < \frac{1}{Z_1 + Z_2} \frac{\hbar^2}{me^2}$$

is of no importance, since in this region the value of $(\varphi_1(0) - \varphi_1(R))$ itself is very small in comparison with the other terms in (6).

Setting (13) equal to the energy of relative motion of the colliding atoms, we obtain the distance R of the minimum approach of the nuclei. For example, for the collision of neon and argon atoms when the energy of the relative motion is 5×10^3 ev, we obtain, according to (13), $R = 2 \times 10^{-9}$ cm. For a pure Coulomb interaction, we would have obtained $R = 5.2 \times 10^{-9}$ cm, and, according to (4), $R = 0.8 \times 10^{-9}$ cm.

For the ionized atoms in (13), we must replace $\chi(x)$ by the corresponding function $\chi_i(x)$ of the ionized atom with the nuclear charge $(Z_1 + Z_2)e$ and add the constant

$$Z_1 Z_2 (Z_1 + Z_2)^{1/3} \frac{me^4}{\hbar^2} (1{,}8 - \alpha) - \Delta E_i,$$

where

$$\alpha = -\left(\frac{d\chi(x)}{dx} - \frac{d\chi_i(x)}{dx}\right)_{x \to 0},$$

and ΔE_i is the difference in ionization potentials of the atom having the [charge] number $(Z_1 + Z_2)$ and of the ionized Z_1 or Z_2 atom.

If the number of distant electrons $z \ll (Z_1 + Z_2)$, then, within the boundaries of the atom, $U_i(R)$ almost coincides with $U(R)$ for the neutral atoms. This is natural, because the processes occurring with the valence electrons cannot change the atomic interaction much when the distance between the nuclei is $R \ll 10^{-8}$ cm.

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